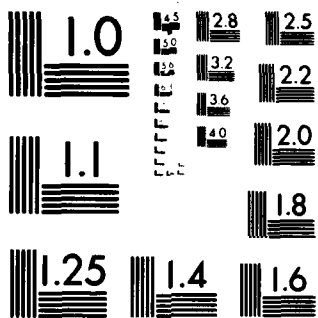


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ORGANOMETALLIC PHOSPHAZENES: SYNTHESIS AND REARRANGEMENT OF
PROPYNYL AND PROPADIENYL CYCLOTRIPHOSHAZENES

by

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Prepared for publication in the Journal
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Organometallic Phosphazenes: Synthesis and Rearrangement of
Propynyl and Propadienyl Cyclotriphosphazenes

H. R. Allcock,* P. J. Harris, and R. A. Nissan

Contribution from the Department of Chemistry, The Pennsylvania
State University, University Park, Pennsylvania 16802. Received

Abstract: A new series of 1,1-dialkyltetrachlorocyclotriphosphazenes with prop-2-ynyl (VI), prop-1,2-dienyl (V), and prop-1-ynyl (XII) substituents have been prepared. These syntheses involve the reactions of copper- (II) or lithio- (IX) phosphazene anions with prop-2-ynyl bromide which lead initially to the formation of the prop-2-ynyl complexes (VI). The prop-2-ynyl side group was found to undergo an alumina-initiated rearrangement to the prop-1,2-dienyl group (V), and both compounds VI and V were found to undergo a methyllithium-initiated rearrangement to the prop-1-ynyl derivatives (XII). These organometallic-initiated rearrangements were monitored by ^{31}P NMR spectroscopy. The structural characterization of all the new compounds is described, and the NMR results, together with the various rearrangements, are discussed in terms of electronic interactions between the C_3H_3 group and the phosphazene ring. The formation of the lithio-phosphazene anion (IX, $\text{R} = \text{CH}_3$) was studied by low temperature ^{31}P NMR spectroscopy, and the results are discussed in terms of the electron distribution within the phosphazene ring.

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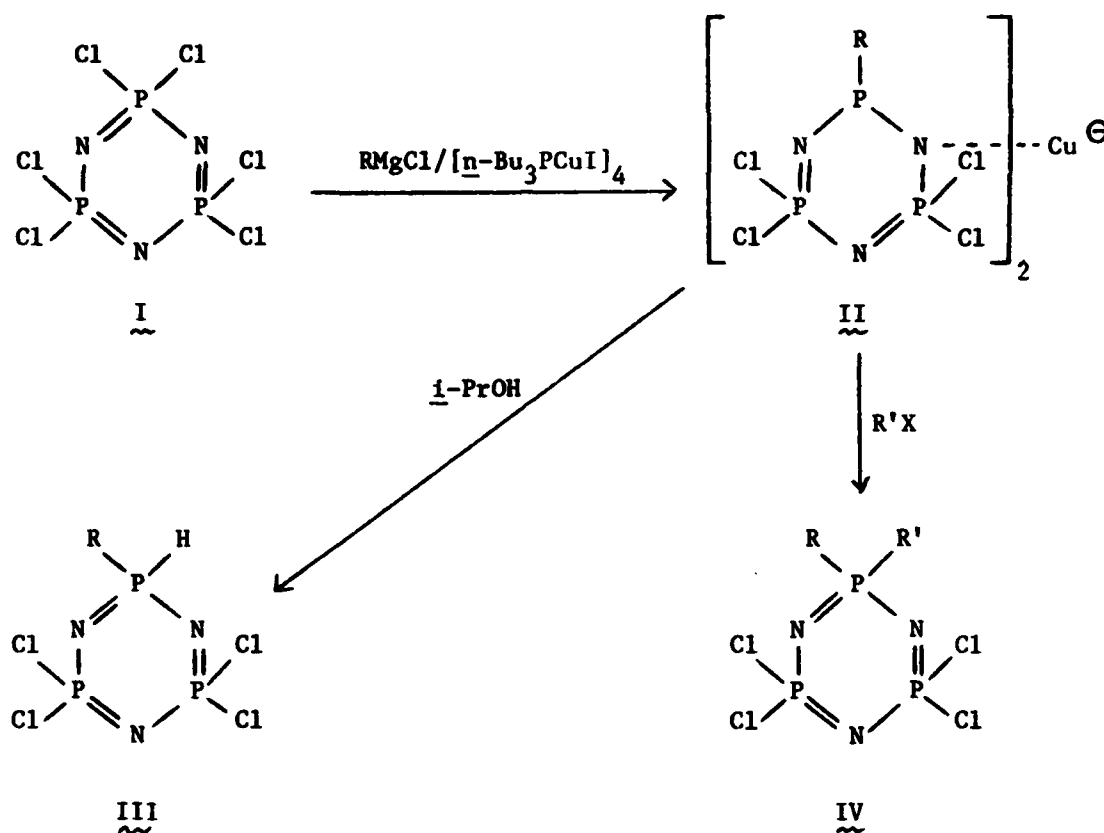
The synthesis of phosphazene compounds with organic substituents bound to the skeleton through direct phosphorus-carbon bonds has received considerable attention in recent years.²⁻⁶ One class of phosphazene compounds of particular interest are those that contain unsaturated organic substituents.⁵⁻⁸ Olefinic or acetylenic side groups can serve as sites for many different types of organic transformations, or as building blocks for polymerization or oligomerization reactions.⁷ Recently, we have also demonstrated the use of acetylenic phosphazenes as ligands for transition metals.⁹

The general route employed for the synthesis of this class of compounds has, until now, involved the reactions of organometallic reagents with halophosphazenes,^{2-4,7,8} a procedure that is often accompanied by side reactions such as ring coupling or skeletal cleavage.^{2-4,7,8}

In this paper we describe a new route for the synthesis of organo-substituted phosphazenes with acetylenic side groups. The approach taken involves the reaction of various metallophosphazene intermediates^{5,6,10,11} with the unsaturated electrophile prop-2-ynyl bromide. The main advantage of this reaction route over the conventional organometallic approach is that the side reactions that lead to phosphazene degradation can be virtually eliminated.

RESULTS AND DISCUSSION

The Primary Reaction. In recent publications we described the synthesis^{10,11} and subsequent reactions^{5,6,10,11} of a new group of metallophosphazene complexes, of general formula, II. These metallophosphazenes (II, R = CH₃, C₂H₅, n-C₃H₇, n-C₄H₉, i-C₃H₇, i-C₄H₉, t-C₄H₉, or allyl) can be synthesized readily by the reaction of hexachlorocyclotriphosphazene, I, with the appropriate Grignard reagent in the presence of [n-Bu₃PCuI]₄.¹⁰

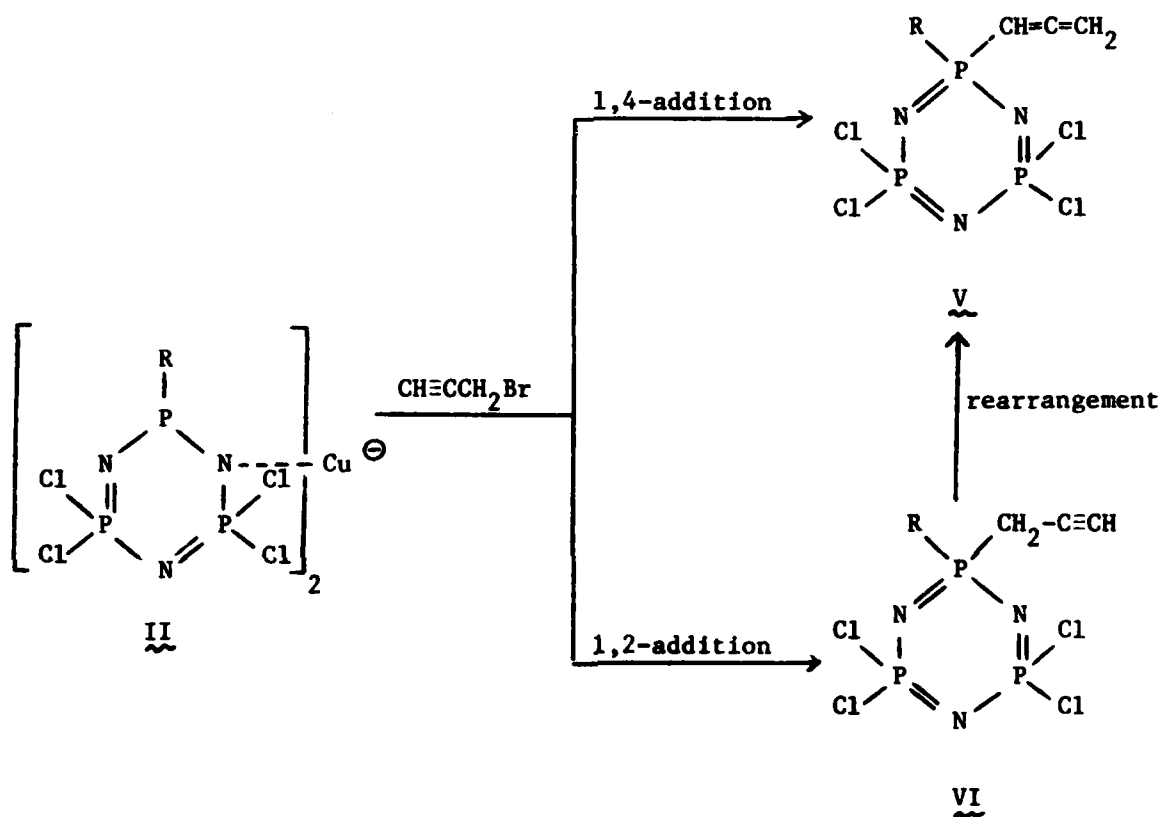


Scheme 1

Subsequent reaction of complexes of type II with *iso*-propanol yields hydrido-phosphazenes, III,^{10,11} while reaction with alkyl halides leads to 1,1-dialkylphosphazenes, IV (Scheme 1).^{5,6}

In this present work, metallophosphazenes of type II were allowed to react with prop-2-ynyl bromide. These reactions were found to yield mixtures of compounds V and VI, ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{n-C}_3\text{H}_7, \text{n-C}_4\text{H}_9, \text{i-C}_3\text{H}_7, \text{i-C}_4\text{H}_9, \text{t-C}_4\text{H}_9$, or allyl). Compounds VI possess a prop-2-ynyl group bound to the phosphazene ring, whereas compounds V contain a prop-1,2-dienyl substituent. The ratio of these two species appeared to be dependent not only on the type of alkyl group, R, bound to the metallophosphazene in II, but also on the isolation and

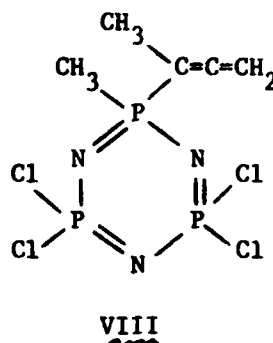
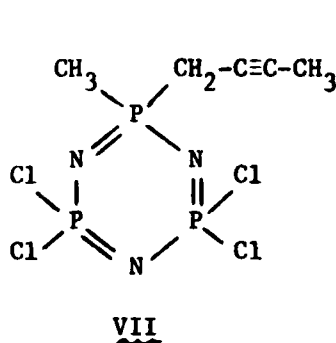
purification procedure employed. These products could result from the reaction of prop-2-ynyl bromide with II in one of two ways, as shown in Scheme 2. The



Scheme 2

initial reaction between metallophosphazene II and the electrophile could occur (a) by competing 1,2- or 1,4- modes of addition,¹² or (b) by simple 1,2-addition⁶ to yield VI, followed by a rearrangement of the prop-2-ynyl side unit to the prop-1,2-dienyl group.¹³ This type of rearrangement could be catalyzed either by copper (I) salts¹³ present in solution, or by neutral alumina.¹³ (Filtration of the products through neutral alumina is a necessary step to remove unwanted copper salts from the products).⁶

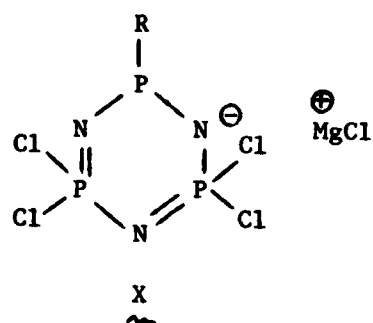
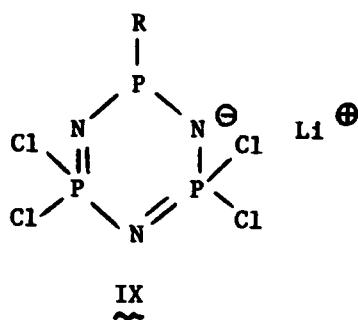
Subsequent experiments were carried out in an attempt to distinguish between these two pathways. In order to explore possibility (a), the metallophosphazene II ($R = CH_3$) was allowed to react with but-2-ynyl bromide. This reaction was chosen for the followings reasons. Earlier work⁵ had shown that the reaction of metallophosphazene II ($R = CH_3$) with prop-2-ynyl bromide led almost exclusively to the prop-1,2-dienyl compound V ($R = CH_3$). Although 1,4-conjugate addition to but-2-ynyl bromide may be somewhat more sterically hindered than with prop-2-ynyl bromide, at least a small amount of this type of product would be expected if the conjugate addition pathway were indeed operative. However, the only product isolated from the reaction of II ($R = CH_3$) with but-2-ynyl bromide was VII. No products such as VIII, derived from



a conjugate addition type reaction, were observed. This result suggests that conjugate addition does not occur during the reaction of metallophosphazenes, II, with acetylenic halides. Thus, it appears that compounds V are formed from compounds VI either by a copper(I) catalyzed rearrangement, or during the isolation procedure. This prospect will be discussed in a later section.

Synthesis of Lithio- and Magnesio-Phosphazenes. In view of the results obtained with copper-phosphazenes, it became clear that the synthesis of prop-2-ynyl substituted phosphazenes VI in a pure state required the use of a metallophosphazene species that did not contain copper. This was achieved by

the low temperature metallation¹⁴ of hydridophosphazenes III with methyl-lithium to yield IX (or with methylmagnesium chloride to yield X).

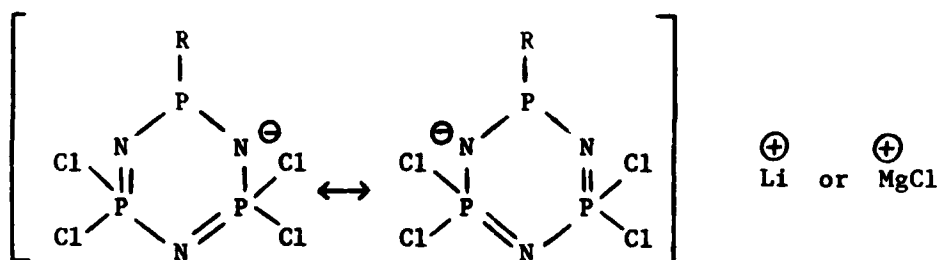


Although both of these new types of metallophosphazenes were extremely reactive and decomposed if warmed to room temperature, it was possible to obtain the ³¹P NMR spectrum of compound IX (R=CH₃) by generating the compound in the cooled probe of an NMR spectrometer.¹⁵

A typical series of spectra are shown in Figure 1. The initial spectrum, a, contains resonances at 17.6 ppm and 13.8 ppm, assigned to the starting material III (R = CH₃).^{10,16} Spectrum b was derived from the reaction mixture after addition of $\approx 1/2$ equivalent of methyllithium, and spectrum c was obtained after addition of ≥ 1 equivalent. Spectrum c, assigned to compound IX (R=CH₃), was interpreted as an AX₂ spin system.¹⁷ The resonance for the phosphorus atom bound to the alkyl group occurred at 97.1 ppm as a triplet ($J_{\text{PNP}} = 93$ Hz). The position of resonance for this nucleus displayed a large downfield shift compared to the parent compound, and appeared in the same general region as for alkyl diamino-phosphines, R'P(NR₂)₂.¹⁸ The resonance assigned to the PCl₂ nuclei occurred at 2.9 ppm as a doublet ($J_{\text{PNP}} = 93$ Hz). This position of resonance is shifted upfield from that of the parent hydrido-phosphazene, and this is presumed to result from a negative charge build-up in the phosphazene ring. The phenomenon can be rationalized in terms of the variation in π electron density distribution

about the phosphazene ring by consideration of the "island" theory of bonding in phosphazene molecules.^{19,20} A build-up of negative charge in one of the P-N-P islands will concentrate toward the end of the island bearing the most electronegative substituents, i.e. the PCl_2 groups. This effect would cause a greater magnetic shielding and thus generate an upfield shift for the position of this nucleus. This type of perturbation of the phosphazene π bonding system has been discussed before,⁶ and can be detected from crystal structure data for various phosphazenes.²¹⁻²⁴

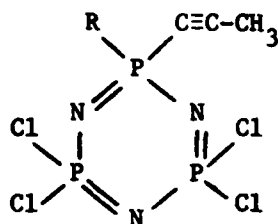
These results can be rationalized best if the metallophosphazenes IX (and X) are viewed as resonance hybrids of the canonical forms described in XI, with the negative charge symmetrically distributed about the N-(R)P-N segment of the phosphazene ring.



XI

Reaction of Lithio- or Magnesio-Phosphazenes with Prop-2-ynyl Bromide.

The extremely high reactivity of compounds IX or X precluded their isolation. However, if these complexes were generated by the reaction of methyllithium (or methylmagnesium chloride) with the hydridophosphazenes III, and were then immediately allowed to react with prop-2-ynyl bromide, the products isolated were either compounds V, VI, or XII. (In each case $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{n-C}_3\text{H}_7$,



XII

n -C₄H₉, i -C₃H₇, i -C₄H₉, t -C₄H₉, or allyl). The specific products, or mixture of products, isolated from these reactions were found to be dependent on the amount of organometallic reagent used for the metallation of the hydrido-phosphazenes, and on the reaction time. Thus, if the metallation reactions were carried out with a deficiency of the organometallic reagent, the final products isolated were always compounds VI. On the other hand, if the metallation reactions were effected with a slight excess of the organometallic reagent, the products consisted of mixtures of compounds V, VI, and XII. However, if these reaction mixtures were stirred at low temperatures for prolonged periods of time, compounds XII could be isolated in pure form in high yield. These results again suggested that a rearrangement of the prop-2-ynyl side group occurs in these reactions. However, in this case, the rearrangement was apparently initiated by an excess of the organometallic reagent used to generate the metallophosphazene. This prospect is considered in the following sections.

The Prop-2-ynyl and Prop-1,2-dienyl Rearrangements. As discussed earlier, the first type of rearrangement observed was that of the prop-2-ynyl compounds, VI, to the prop-1,2-dienyl compounds, V, a rearrangement apparently catalyzed either by copper(I) salts or by neutral alumina. The second type was of compounds VI to XII, apparently via V. This rearrangement appeared to be initiated by an organometallic reagent. The following series of experiments

were carried out in an attempt to determine the exact course of these different rearrangements.

A pure sample of each of the prop-2-ynyl compounds VI ($R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_3H_7, i-C_4H_9, t-C_4H_9$, or allyl) were synthesized via the reaction of the corresponding lithiophosphazene IX with prop-2-ynyl bromide (see Experimental section). These compounds were then allowed to react with $[n-Bu_3PCuI]_4$. These reactions were carried out to explore the possibility that the rearrangement of compounds VI to V was catalyzed by copper(I) species. At the end of a 24 h period, no prop-1,2-dienyl substituted compounds were observed.

In a second series of reactions, pure samples of compounds VI were dissolved in CH_2Cl_2 and filtered through neutral alumina. After this procedure had been repeated 2-3 times, complete rearrangement of the side groups to the prop-1,2-dienyl compounds V had occurred. This procedure allowed the isolation of all compounds V ($R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_3H_7, i-C_4H_9, t-C_4H_9$, or allyl) in pure form. These results demonstrated conclusively that the rearrangement of compounds VI to V was catalyzed by neutral alumina and not by copper(I) salts.

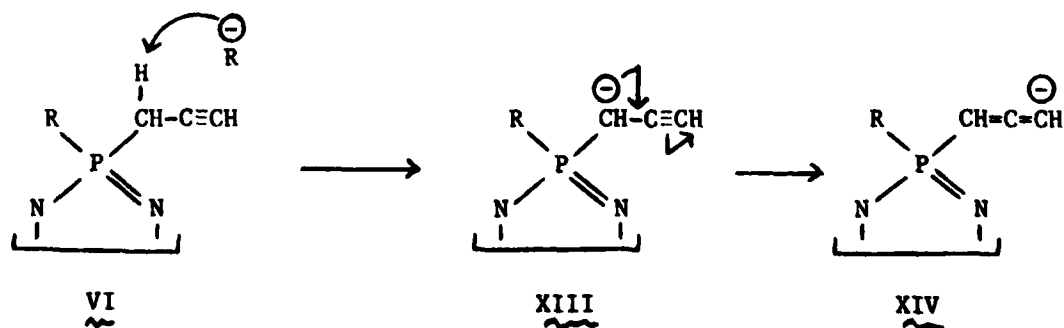
The rearrangement of a terminal acetylene group to an allene, initiated simply by alumina, has been observed only in a limited number of cases.²⁵⁻²⁸ The hydrogen atom involved in the migration must initially be adjacent to a second multiply bonded atom,^{25,26} or adjacent to any functional group which will increase its acidity.^{27,28} It is possible that both these factors are important in the rearrangement of the prop-2-ynyl phosphazenes VI to the prop-1,2-dienyl substituted compounds V. The activation of the protons of a methyl or methylene group attached to a phosphazene ring²⁹ or phosphoryl

group³⁰ is well-documented and has been attributed to d-orbital interactions. The possibility also exists of an electronic interaction between the prop-1,2-dienyl group and the phosphazene skeleton.³¹⁻³³

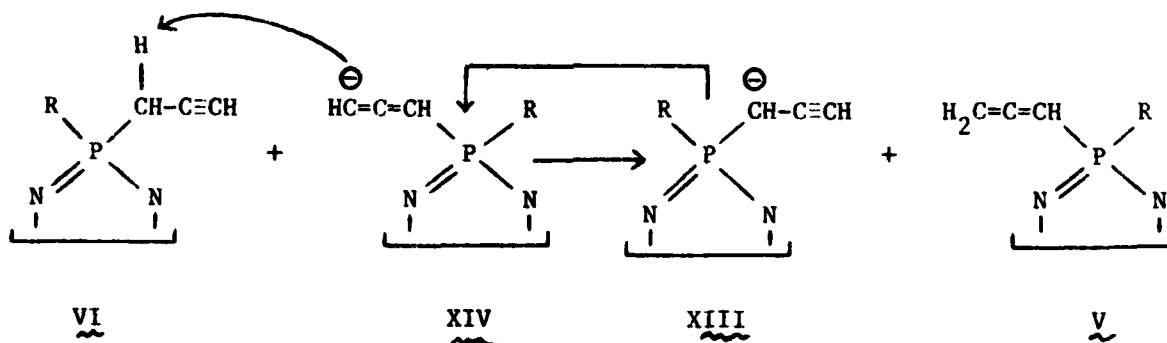
The Prop-2-ynyl to Prop-1-ynyl Rearrangement. Peripheral observations had suggested that this type of rearrangement reaction was initiated by traces of organometallic reagents. This possibility was explored by the following series of experiments. A pure sample of compound VI ($R = CH_3$) was treated with a small quantity of methyllithium. The reaction was monitored by ^{31}P NMR spectroscopy,¹⁵ and a typical series of spectra are shown in Figure 2. The initial spectrum, a, shows resonances at 34.3 ppm (triplet) and 19.4 ppm (doublet),¹⁶ assigned to the starting material VI, $R = CH_3$ (see Table II). This spectrum was obtained before the addition of any organometallic reagent. A small quantity of methyllithium was then introduced into the NMR tube, and the ^{31}P NMR spectrum was scanned at intervals. As the reaction proceeded, peaks at 25.9 ppm (triplet) and 18.6 (doublet) (spectra b and c) appeared. These resonances were assigned to the prop-1,2-dienyl substituted compound V ($R = CH_3$). After nearly all of the starting material had been consumed (spectrum c), peaks at 18.8 ppm (doublet) and 2.5 ppm (triplet) began to appear (spectra d and e). These resonances were assigned to the prop-1-ynyl compound XII, ($R = CH_3$). After completion of the reaction (spectrum f), the only resonances present were those assigned to compound XII ($R = CH_3$). Thus, it was concluded that complete rearrangement of the prop-2-ynyl compound VI ($R = CH_3$) to the prop-1-ynyl compound V ($R = CH_3$) had occurred, probably via an intermediate formation of the prop-1,2-dienyl complex V ($R = CH_3$).

The Prop-1,2-dienyl to Prop-1-ynyl Rearrangement. The possibility that the prop-1,2-dienyl compounds V were intermediates in the rearrangement of compounds VI to XII was explored by the following experiment. A pure sample of compound V ($R = \text{CH}_3$) was treated with a small quantity of methyl-lithium. Again the reaction was monitored by ^{31}P NMR spectroscopy;¹⁵ a typical series of spectra are shown in Figure 3. The initial spectrum, a, showed resonances at 25.9 ppm (triplet) and 18.6 (doublet)¹⁶ assigned to starting material V ($R = \text{CH}_3$). A small quantity of methyllithium was then introduced into the mixture and, again, the spectrum was recorded at intervals. As the reaction proceeded (spectra b, c, and d), the only new peaks that appeared were at 18.8 ppm (doublet) and 2.5 ppm (triplet), assigned to the prop-1-ynyl compound XII ($R = \text{CH}_3$). Thus, it is clear that the prop-1,2-dienyl compounds V are indeed intermediates in the organometallic initiated rearrangement of prop-2-ynyl phosphazenes VI to prop-1-ynyl compounds XII.

These rearrangements probably occur via the following mechanism. The initiation step involves abstraction of the proton adjacent to the phosphazene ring²⁹ in compounds VI by the organometallic reagent to yield the phosphazene carbanion, XIII. This compound undergoes a rearrangement¹³ to the allenic carbanion, XIV. As the organometallic reagent is present in low concentrations only, it is consumed rapidly. At this stage, the reaction is thought to proceed

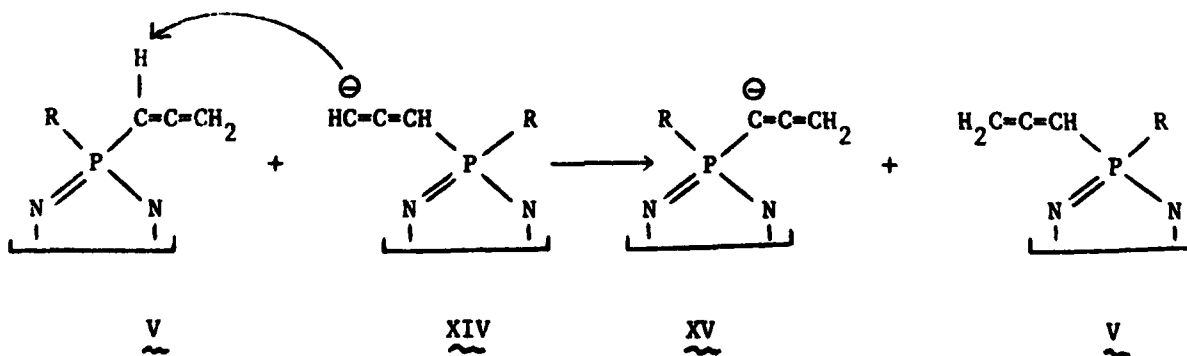


as follows. The propagation step in the rearrangement sequence involves the allenic carbanion, XIV. This species now acts as the base and abstracts the acidic proton from compound VI to yield the prop-1,2-dienyl substituted phosphazene V and more of the phosphazene carbanion, XIII. This species again rearranges to the allenic carbanion XIV, and the reaction proceeds.

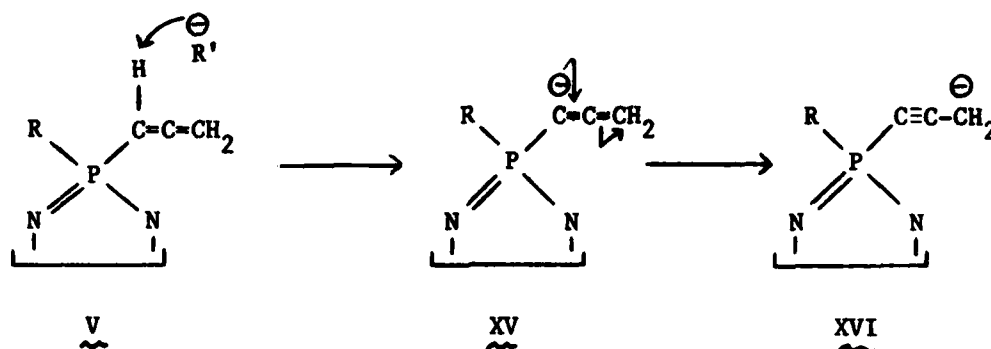


This sequence continues until only low concentrations of compound VI remain. This was clearly demonstrated by the ^{31}P NMR study of the reaction (Figure 1, spectrum c).

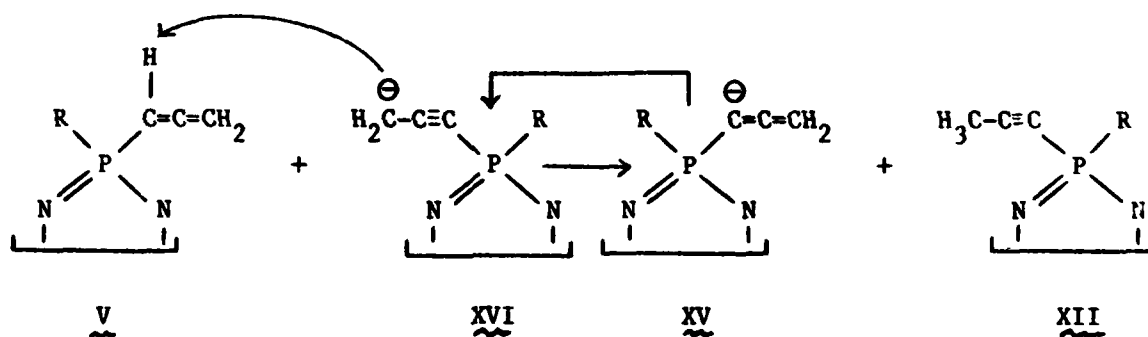
At this stage, the allenic carbanion, XIV, is thought to abstract the less acidic proton adjacent to the phosphazene ring in the prop-1,2-dienyl compound, V, to yield carbanion XV. This intermediate was also generated via the reaction of the prop-1,2-dienyl compound with methyllithium.



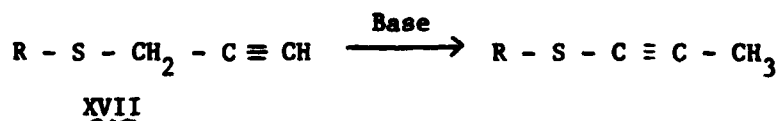
Carbanion XV then undergoes further rearrangement to yield carbanion XVI.



The final step in the rearrangement sequence involves abstraction of the proton from the prop-1,2-dienyl compound V by anion XVI to generate the final product, the prop-1-ynyl substituted phosphazene XII.



A related process has been observed^{34,35} in the rearrangement of the acetylenic substituted thio-ethers, XVII. However, in these cases, the reaction is reversible. All attempts to reverse the prop-2-ynyl \rightarrow prop-1-ynyl



rearrangement observed here have been unsuccessful. This failure is perhaps due to an electronic interaction between the acetylene group and the phosphazene ring in compounds XII, a possibility that will be considered in a forthcoming publication.

Proof of Structure of Compounds V, VI, and XII. All new phosphazene compounds synthesized in this study were characterized by infrared and ^1H , ^{13}C and ^{31}P NMR spectroscopy, mass spectrometry (low and high resolution) and, in representative cases, by elemental analysis. These data are listed in Tables I-IV.

The mass spectral data³⁶ for all compounds V, VI, XII ($\text{R} = \text{CH}_3$, C_2H_5 , $n\text{-C}_3\text{H}_7$, C_4H_9 , $i\text{-C}_3\text{H}_7$, $1\text{-C}_4\text{H}_9$, or allyl) and VII synthesized in this work are listed in Table I. All compounds displayed a strong parent ion with a characteristic Cl_4 isotope pattern. The fragmentation pathways observed involved loss of alkyl and C_3H_3 groups as well as chlorine. However, from the interpretation of these data, it was impossible to distinguish between isomers of structure V, VI, and XII.

The infrared spectra³⁷ of all compounds V, VI, VII, and XII were consistent with the proposed structures. In each case an intense absorbance between 1100 and 1300 cm^{-1} was observed, a characteristic of the PN skeleton in cyclic phosphazene compounds.²⁸ The $\text{C}\equiv\text{C}$ absorbance³⁹ for the prop-2-ynyl compounds, VI, and the prop-1-ynyl, XII, was observed between 2010 and 2120 cm^{-1} , but in most cases it was extremely weak. However, the absorbance assigned to the $\text{C}=\text{C}=\text{C}$ stretch for compounds XII (between 1930 and 1980 cm^{-1})³⁹ was always relatively intense and proved extremely useful in the identification of these compounds. Other bands in the infrared spectra of all compounds V, VI, VII, and XII were tentatively assigned to C-H, P-C, C-C, and P-Cl absorbances.^{6, 39}

The ^{31}P NMR spectra^{15, 16} of compounds V, VI, VII, and XII (listed in Table II) were all interpreted as simple AB_2 spin systems.¹⁷ The resonance for the phosphorus atom bound to the alkyl groups appeared as a triplet in the

proton decoupled spectra. However, these resonances broadened in the proton undecoupled ^{31}P NMR spectra, due to unresolved proton-phosphorus couplings. By contrast, the other resonances observed in these spectra, a doublet, centered between 20.5 ppm and 18.6 ppm and assigned to the PCl_2 groups, remained virtually unaffected following removal of the proton decoupling frequencies.

It is of interest that a dramatic ^{31}P upfield shift (and in some cases an increase in the P-P coupling constant) of the alkylated phosphorus accompanied the rearrangement of the C_3H_3 group from prop-2-ynyl to prop-1-ynyl. Thus, for the series VI, V, XII ($\text{R} = \text{CH}_3$), the phosphorus resonance for the prop-2-ynyl derivative occurred at 34.3 ppm, the prop-1,2-dienyl compound occurred at 25.9 ppm and the prop-1-ynyl complex occurred at 2.5 ppm. This effect is perhaps a consequence of electronic interactions between the prop-1,2-dienyl group or the prop-1-ynyl group and the π system of the phosphazene ring.³¹⁻³³ An X-ray crystal structure analysis, currently under way, will help to clarify this point.

The alkyl groups bound to the phosphazene ring in compounds V, VI, VII and XII were all characterized by a combination of ^1H and ^{13}C NMR spectroscopy. The ^1H NMR data⁴⁰ are listed in Table III; the ^{13}C NMR data⁴¹ are listed in Table IV. In some cases, from an interpretation of the ^1H NMR data, it was possible to distinguish between complexes V, VI, and XII. In many cases, however, the ^1H NMR spectra appeared as a complex pattern of overlapping resonances that could not be interpreted easily. By contrast, analysis of the ^{13}C NMR spectra of all compounds synthesized in this work provided a complete proof of structure. Certain trends appear to be consistent throughout the data sets. The resonances for the carbon atoms bonded directly to the

phosphazene ring always appeared as a doublet of triplets,⁶ due to coupling to the near (J_{PC}) and remote (J_{PNPC}) phosphorus nuclei. Resonances for carbon atoms two or three bonds removed from the phosphazene ring appeared as doublets in most cases. For the series of compounds VI, V, and XII ($R = CH_3$), the chemical shift of the methyl group carbon atom increased from 17.6 ppm for the prop-2-ynyl compound to 20.0 ppm for the prop-1,2-dienyl compound to 23.2 ppm for the prop-1-ynyl complex. The values of the coupling constants J_{PC} and J_{PNPC} for this methyl carbon, as well as the α carbon of the C_3H_3 group, also increase in this order. For the α carbon atom of the C_3H_3 group, the increase in J_{PC} is quite dramatic. This value increases from 88.8 Hz for the prop-2-ynyl compound, to 131.7 Hz for the prop-1,2-dienyl derivative, to 213.9 Hz for the prop-1-ynyl complex.

All these effects can be rationalized in terms of increasing electronic interactions between the C_3H_3 substituent and the phosphazene ring.³¹⁻³³ For the series of compounds VI ($R = CH_3, C_2H_5, i-C_3H_7, t-C_4H_9$), the chemical shift of the α carbon of the prop-2-ynyl substituent decreased from 25.5 ppm ($R = CH_3$) to 24.2 ppm ($R = C_2H_5$) to 22.1 ppm ($R = i-C_3H_7$) to 19.4 ppm ($R = t-C_4H_9$). These results can be rationalized simply in terms of the electron donating ability of the alkyl group.⁴² This increases the electron density at phosphorus and thus increases the shielding effect at the α carbon of the C_3H_3 group. Thus, it is clear that the ^{13}C NMR spectra of alkyl substituted phosphazene compounds contain valuable information about the various interactions between the phosphazene ring and the organic side group.

EXPERIMENTAL SECTION

Materials. Hexachlorocyclotriphosphazene was supplied by Ethyl Corp. and was purified by sublimation, followed by two recrystallizations from n-hexane. Organometallic reagents were obtained from Aldrich or Alfa-Ventron. Prop-2-ynyl bromide (Aldrich) was used without further purification. Tetrahydrofuran (Fisher) was distilled into the reaction flask under an atmosphere of dry nitrogen from sodium-benzophenone ketyl drying agent. The reagents, $[\underline{n}\text{-Bu}_3\text{PCuI}]_4$ ⁴³ and but-2-ynyl bromide⁴⁴ were synthesized by published procedures. All manipulations involving organometallic reagents or air-sensitive intermediates were carried out under an atmosphere of dry nitrogen.

Synthesis of Copper Phosphazenes (II). The metallophosphazenes, II, were all synthesized in an identical manner:^{6,10} Hexachlorocyclotriphosphazene (I) (5.0 g, 0.014 mol) and $[\underline{n}\text{-Bu}_3\text{PCuI}]_4$ (4.0 g, 0.0025 mol) were stirred together in THF (150 mL) at -78°C. The Grignard reagent (25 mL of a 3M solution in diethyl ether or THF) was added dropwise over a period of ≈ 30 min.. This reaction mixture was then stirred for 16 h and the temperature was allowed to rise slowly to $\approx 25^\circ\text{C}$. These complexes were not isolated, but were allowed to react in situ, as described in the following sections.

Synthesis of Hydrido-Phosphazenes (III). These compounds were prepared from the copper-phosphazenes (II) by published procedures.^{10,11} Compounds III ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \underline{n}\text{-C}_3\text{H}_7, \underline{n}\text{-C}_4\text{H}_9, \underline{i}\text{-C}_3\text{H}_7$) were sublimed from the reaction mixture, as described previously. Compounds III ($\text{R} = \underline{i}\text{-C}_4\text{H}_9, \underline{t}\text{-C}_4\text{H}_9, \text{allyl}$) were distilled from the reaction residue at 120° under reduced pressure.

Synthesis of Prop-1,2-dienyl Compounds (V). A solution of prop-2-ynyl bromide (80% in toluene, 5 mL) was added dropwise to a solution of the copper

phosphazene (II) prepared as described previously. The reaction mixture was then stirred for 24 h. The solvent was removed under reduced pressure and the products were dissolved in toluene (250 mL). The organic layer was then washed with aqueous HCl (10% solution, 250 mL), dried over MgSO_4 , and the solvent was removed under reduced pressure to leave the crude product. This mixture was purified by filtration of a solution in CH_2Cl_2 through neutral alumina, followed by recrystallization from n-hexane to leave the product as white crystals. In some cases filtration of the CH_2Cl_2 solution through neutral alumina had to be repeated two or three times to effect complete conversion to the prop-1,2-dienyl substituted compound.

Synthesis of Lithio- and Magnesio-Phosphazenes. All of these compounds were prepared in an identical manner. The following is a typical procedure: Methylhydridotetrachlorocyclotriphosphazene (III, $\text{R} = \text{CH}_3$) (5.0 g, 0.017 mol), prepared as described previously, was dissolved in THF (150 mL) and the solution was cooled to -78°C . Methyl lithium (as a lithium bromide complex, 11 mL of a 1.5 M solution in diethyl ether, 0.016 mol) or methyl magnesium chloride (5.5 mL of a 3M solution in THF, 0.016 mol) was then added carefully. The temperature of the reaction mixture during addition of the organometallic reagent was not allowed to rise above -70°C . This mixture was then stirred for a further 30 min at -78°C . These complexes were not isolated but were reacted in situ, as described in the following sections.

Preparation of Prop-2-ynyl Compounds (VI). A solution of prop-2-ynyl bromide (3 mL, 80% solution in toluene) was added rapidly to the solution of lithio- or magnesio-phosphazene, synthesized as described in the preceding section. The mixture was then stirred for 2 h during which time the temperature was allowed to warm to 25°C . The solvent was then removed under vacuum, and

the products were extracted with hot hexane (4 x 50 mL portions). The resultant hexane layer was concentrated by removal of some of the solvent under vacuum and recrystallization at -10°C left the product as white crystals.

Preparation of Prop-1-ynyl Compounds (XII). A solution of the lithio- or magnesio-phosphazene was prepared as described previously, except that 15 mL of the methyllithium reagent (0.023 mol) or 7.7 mL of the methyl magnesium chloride solution (0.023 mol) were used. A solution of prop-2-ynyl bromide (3 mL, 80% in toluene) was added slowly to this solution and the mixture was stirred at -80°C for 6 h. The temperature was then allowed to rise to 25°C and the solvent was removed under vacuum. The products were extracted with hot hexane (4 x 50 mL portions) and were recrystallized from n-hexane.

Attempted Copper-Initiated Rearrangement of Prop-2-ynyl Substituted Phosphazenes (VI) to Prop-1,2-dienyl Substituted Complexes (V). A pure sample of the prop-2-ynyl substituted phosphazene (VI) (100 mg, ≈ 0.3 mmol) and $[\text{n-Bu}_3\text{PCuI}]_4$ (20 mg, 0.012 mmol) were dissolved in CDCl_3 (1 mL) and the solution was filtered into an NMR tube. The ^1H NMR spectrum of this mixture showed only resonances in the region 1-2.5 δ . No olefinic proton resonances corresponding to the prop-1,2-dienyl compound were observed. This mixture was allowed to stand for 24 h. At the end of this time the ^1H NMR spectrum was rescanned. No difference existed between this spectrum and the initial spectrum. Thus, it was concluded that no rearrangement of the C_3H_3 side group had occurred.

The Alumina Initiated Rearrangement of Prop-2-ynyl Substituted Phosphazenes (VI) to Prop-1,2-dienyl Substituted Phosphazenes (V). A pure sample of the prop-2-ynyl substituted phosphazene (VI) (1.0 g, ≈ 2.80 mmol) was dissolved in

CH_2Cl_2 (10 mL). This solution was introduced on to a chromatography column (2.5 cm x 7 cm) packed with neutral alumina (Brockman Activity I) and eluted with CH_2Cl_2 (200 mL). The product was isolated by removal of the solvent under vacuum. The filtration through alumina was repeated two or three times to bring about complete conversion to the prop-1,2-dienyl complex. These compounds were then recrystallized from n-hexane.

Organometallic-Initiated Rearrangement of Prop-2-ynyl Substituted Phosphazenes (V) to Prop-1-ynyl Substituted Derivatives (XII). Pure prop-2-ynyl substituted phosphazenes (VI) (1.0 g, ≈ 2.8 mmol) were dissolved in THF (50 mL) and the solutions were cooled to -78°C . Methylolithium (0.20 mL, as a lithium bromide complex, 1.5 M in diethyl ether) was then introduced into the reaction vessel and the mixture was stirred at -78°C for 4 h.. At the end of this time the temperature of the reaction mixture was slowly allowed to rise to 25°C and the solvent was removed under vacuum. The products were dissolved in n-hexane, filtered, and recrystallized to leave the prop-1-ynyl substituted phosphazenes (XII) as white crystals. Typical yields were 90-96%.

Organometallic-Initiated Rearrangement of Prop-1,2-dienyl Phosphazenes (V) to Prop-1-ynyl Substituted Complexes (XII). A pure sample of the prop-1,2-dienyl substituted phosphazene compounds (V) (1.0 g, ≈ 2.8 mmol) was dissolved in THF (50 mL) and the solution was cooled to -78°C . A solution of methylolithium (as a lithium bromide complex, 0.20 mL, 1.5 M solution in diethyl ether) was then added to the phosphazene solution and the mixture was stirred for 6 h at -78°C . At the end of this time the temperature was allowed to rise to 25°C and the solvent was removed under vacuum. The products were dissolved in hexane and filtered. The final product, the prop-1-ynyl substituted phosphazenes (XII), were isolated by recrystallization from n-hexane. Typical yields were

90-95%.

³¹P NMR Monitoring of the Rearrangement of the Prop-2-ynyl Phosphazene

to the Prop-1-ynyl Complex. A pure sample of the prop-2-ynyl phosphazene (VI, R = CH₃) (0.10 g, 0.3 mmol) was dissolved in a mixture of THF - d₈ (0.5 mL) and THF (1.5 mL) and filtered into an NMR tube (10 mm. OD) under an atmosphere of dry nitrogen. (The deuterio-compound was needed as an NMR lock). The tube was then sealed with a septum cap. The sample was introduced into the probe of the spectrometer and the temperature was gradually lowered to -70°C. The spectrum was then scanned. An aliquot of methyllithium (0.1 mL, as a lithium bromide complex, 1.5M solution in diethyl ether) was then syringed into the NMR tube through the septum. Any methane gas evolved was vented from the tube with a second syringe needle. The spectrum was then rescanned at intervals.

³¹P NMR Monitoring of the Rearrangement of the Prop-1,2-dienyl Phosphazene

to the Prop-1-ynyl Phosphazene. This reaction was carried out in an identical manner to the preceding experiment. However, the prop-1,2-dienyl phosphazene, V (R = CH₃) was used.

³¹P NMR Monitoring of the Synthesis of the Lithio-Phosphazene (IX, R = CH₃).

A pure sample of methylhydridotetrachlorocyclotriphosphazene (III, R = CH₃) was dissolved in a mixture of THF - d₈ (0.5 ml) and THF (2.0 ml) and was filtered into an NMR tube (10 mm OD) under an atmosphere of dry nitrogen. The tube was then sealed with a septum cap, was introduced into the NMR probe, and the temperature lowered slowly to -70°C. The spectrum of the sample was obtained. Methyl-lithium (0.25 mL, as a lithium bromide complex, 1.5 M in diethyl ether) was then introduced into the tube with a syringe through the septum cap in 2 or 3 aliquots. Any gas pressure in the tube was vented with a second syringe needle.

The spectrum of the mixture was obtained between each addition of the lithium reagent.

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TABLE I. DIALKYLPHOSPHAZENES. CHARACTERIZATION DATA

COMPOUND	% YIELD ^a	Mp (°C)	MASS SPECTRAL DATA ^b		ELEMENTAL ANALYSIS DATA ^b	
			FOUND	CALCD.	FOUND	CALCD.
$N_3P_3Cl_4(CH_3)(CH_2C\equiv CH)$	95	132	329	329	C 14.61	C 14.50
					H 2.01	H 1.81
					N 12.64	N 12.69
					P 27.91	P 28.10
					Cl 42.73	Cl 42.90
$N_3P_3Cl_4(C_2H_5)(CH_2C\equiv CH)$	93	140	343	343	342.8702	343.8685
$N_3P_3Cl_4(n-C_3H_7)(CH_2C\equiv CH)$	92	170	357	357	356.8843	356.8841
$N_3P_3Cl_4(n-C_4H_9)(CH_2C\equiv CH)$	82	158	371	371	370.9011	370.8997
$N_3P_3Cl_4(i-C_3H_7)(CH_2C\equiv CH)$	88	110	357	357	356.8850	356.8841
$N_3P_3Cl_4(i-C_4H_9)(CH_2C\equiv CH)$	76	122	371	371	370.8977	370.8997
$N_3P_3Cl_4(t-C_4H_9)(CH_2C\equiv CH)$	79	109	371	371	370.9028	370.8997
$N_3P_3Cl_4(C_3H_5)(CH_2C\equiv CH)$	84	153	355	355	354.8681	345.8684
$N_3P_3Cl_4(CH_3)(CH=C=CH_2)$	85	101	329	329	328.8532	328.8528
$N_3P_3Cl_4(C_2H_5)(CH=C=CH_2)$	74	74	343	343	342.8691	342.8685
$N_3P_3Cl_4(n-C_3H_7)(CH=C=CH_2)$	68	85	357	357	356.8848	356.8841
$N_3P_3Cl_4(n-C_4H_9)(CH=C=CH_2)$	62	77	371	371	370.9001	370.8997
$N_3P_3Cl_4(i-C_3H_7)(CH=C=CH_2)$	72	40	357	357	C 20.22	C 20.06
					H 2.81	H 2.79
					N 11.78	N 11.70
					P 25.82	P 25.90
					Cl 39.40	Cl 39.55

TABLE I (continued)

$N_3P_3Cl_4(\underline{i}\text{-}C_4H_9)(CH=C=CH_2)$	55	65	371	371	370.8998	370.8997
$N_3P_3Cl_4(\underline{t}\text{-}C_4H_9)(CH=C=CH_2)$	50	38	371	371	370.8986	370.8997
$N_3P_3Cl_4(C_3H_5)(CH=C=CH_2)$	64	80	355	355	354.8677	354.8684
$N_3P_3Cl_4(CH_3)(C\equiv CCH_3)$	93	75	329	329	328.8535	328.8528
$N_3P_3Cl_4(C_2H_5)(C\equiv CCH_3)$	90	55	343	343	342.8694	342.8685
$N_3P_3Cl_4(\underline{n}\text{-}C_3H_7)(C\equiv CCH_3)$	91	78	357	357	356.8850	356.8841
$N_3P_3Cl_4(\underline{n}\text{-}C_4H_9)(C\equiv CCH_3)$	86	88	371	371	370.8993	370.8997
$N_3P_3Cl_4(\underline{i}\text{-}C_3H_7)(C\equiv CCH_3)$	79	52	357	357	356.8846	356.8841
$N_3P_3Cl_4(\underline{i}\text{-}C_4H_9)(C\equiv CCH_3)$	83	39	371	371	370.9004	370.8997
$N_3P_3Cl_4(\underline{t}\text{-}C_4H_9)(C\equiv CCH_3)$	83	35	371	371	C 22.54	C 22.52
					H 3.27	H 3.22
					N 11.11	N 11.26
					P 24.64	P 24.93
					Cl 38.29	Cl 38.07
$N_3P_3Cl_4(C_3H_5)(C\equiv CCH_3)$	87	55	355	355	354.8680	354.8684
$N_3P_3Cl_4(CH_3)(CH_2C\equiv CCH_3)$	88	170	343	343	342.8681	342.8685

^a Yields of prop-2-ynyl and prop-1-ynyl compounds are from reactions of lithio-phosphazenes with prop-2-ynyl bromide. Yields of prop-1,2-dienyl compounds are from reactions of copper-phosphazenes with prop-2-ynyl bromide after rearrangement on neutral alumina. The yields of prop-2-ynyl and prop-1-ynyl compounds from the reaction of magnesio-phosphazenes with prop-2-ynyl bromide were significantly lower than yields obtained from the lithio-phosphazenes.

^b Mass spectral data are presented for the $^{35}Cl_4$ peak in the parent cluster.

TABLE II. DIALKYLPHOSPHAZENES. ^{31}P NMR DATA^a

COMPOUND	CHEMICAL SHIFT (ppm) ^b		COUPLING CONSTANT J_{PNP} (Hz)
	P(R)_2	P(Cl)_2	
$\text{N}_3\text{P}_3\text{Cl}_4(\text{CH}_3)(\text{CH}_2\text{C}\equiv\text{CH})$	34.3(t)	19.4(d)	6.0
$\text{N}_3\text{P}_3\text{Cl}_4(\text{C}_2\text{H}_5)(\text{CH}_2\text{C}\equiv\text{CH})$	40.3(t)	20.5(d)	<2
$\text{N}_3\text{P}_3\text{Cl}_4(\text{n-C}_3\text{H}_7)(\text{CH}_2\text{C}\equiv\text{CH})$	37.9(t)	19.9(d)	<2
$\text{N}_3\text{P}_3\text{Cl}_4(\text{n-C}_4\text{H}_9)(\text{CH}_2\text{C}\equiv\text{CH})$	38.2(t)	19.7(d)	<2
$\text{N}_3\text{P}_3\text{Cl}_4(\text{i-C}_3\text{H}_7)(\text{CH}_2\text{C}\equiv\text{CH})$	44.5(t)	20.1(d)	<2
$\text{N}_3\text{P}_3\text{Cl}_4(\text{i-C}_4\text{H}_9)(\text{CH}_2\text{C}\equiv\text{CH})$	36.8(t)	19.5(d)	<2
$\text{N}_3\text{P}_3\text{Cl}_4(\text{t-C}_4\text{H}_9)(\text{CH}_2\text{C}\equiv\text{CH})$	49.3(t)	20.7(d)	<2
$\text{N}_3\text{P}_3\text{Cl}_4(\text{C}_3\text{H}_5)(\text{CH}_2\text{C}\equiv\text{CH})$	34.6(t)	19.9(d)	<2
$\text{N}_3\text{P}_3\text{Cl}_4(\text{CH}_3)(\text{CH}=\text{C}=\text{CH}_2)$	25.9(t)	18.6(d)	9.0
$\text{N}_3\text{P}_3\text{Cl}_4(\text{C}_2\text{H}_5)(\text{CH}=\text{C}=\text{CH}_2)$	31.6(t)	19.5(d)	<2
$\text{N}_3\text{P}_3\text{Cl}_4(\text{n-C}_3\text{H}_7)(\text{CH}=\text{C}=\text{CH}_2)$	29.2(t)	18.9(d)	<2
$\text{N}_3\text{P}_3\text{Cl}_4(\text{n-C}_4\text{H}_9)(\text{CH}=\text{C}=\text{CH}_2)$	29.3(t)	18.7(d)	3.0
$\text{N}_3\text{P}_3\text{Cl}_4(\text{i-C}_3\text{H}_7)(\text{CH}=\text{C}=\text{CH}_2)$	35.9(t)	19.0(d)	<2
$\text{N}_3\text{P}_3\text{Cl}_4(\text{i-C}_4\text{H}_9)(\text{CH}=\text{C}=\text{CH}_2)$	28.3(t)	18.5(d)	<2
$\text{N}_3\text{P}_3\text{Cl}_4(\text{t-C}_4\text{H}_9)(\text{CH}=\text{C}=\text{CH}_2)$	39.8(t)	18.9(d)	<2
$\text{N}_3\text{P}_3\text{Cl}_4(\text{C}_3\text{H}_5)(\text{CH}=\text{C}=\text{CH}_2)$	25.8(t)	18.9(d)	<2
$\text{N}_3\text{P}_3\text{Cl}_4(\text{CH}_3)(\text{C}\equiv\text{CCH}_3)$	2.5(t)	18.8(d)	14.0
$\text{N}_3\text{P}_3\text{Cl}_4(\text{C}_2\text{H}_5)(\text{C}\equiv\text{CCH}_3)$	9.9(t)	19.9(d)	14.0
$\text{N}_3\text{P}_3\text{Cl}_4(\text{n-C}_3\text{H}_7)(\text{C}\equiv\text{CCH}_3)$	7.0(t)	19.0(d)	14.0

Table II (continued)

$N_3P_3Cl_4$ ($n-C_4H_9$) ($C\equiv CCH_3$)	7.5(t)	19.2(d)	13.0
$N_3P_3Cl_4$ ($i-C_3H_7$) ($C\equiv CCH_3$)	14.7(t)	19.2(d)	9.2
$N_3P_3Cl_4$ ($i-C_4H_9$) ($C\equiv CCH_3$)	6.4(t)	19.2(d)	13.0
$N_3P_3Cl_4$ ($t-C_4H_9$) ($C\equiv CCH_3$)	20.9(t)	19.7(d)	6.0
$N_3P_3Cl_4$ (C_3H_5) ($C\equiv CCH_3$)	3.7(t)	19.2(d)	15.0
$N_3P_3Cl_4$ (CH_3) ($CH_2C\equiv CCH_3$)	36.3(t)	19.4(d)	<2

^a Samples were dissolved in $CDCl_3$

^b d = doublet, t = triplet

TABLE III. DIALKYLPHOSPHAZENES. ^1H NMR DATA

COMPOUND	CHEMICAL SHIFT (δ) ^a		COUPLING CONSTANTS	
			(Hz) ^b	
$\text{N}_3\text{P}_3\text{Cl}_4(\text{CH}_3)(\text{CH}_2\text{C}\equiv\text{CH})$	$-\text{CH}_3$	1.77 (d, t)	J_{PCH}	= 14.5
			J_{PNPCH}	= 2.5
	$-\text{CH}_2\text{C}\equiv\text{CH}$	2.83 (d, m)	J_{PCH}	= 15.8
			J_{PNPCH}	= 2.0
	$-\text{CH}_2\text{C}\equiv\text{CH}$	2.27 (d, t)	J_{PCCCH}	= 7.2
			J_{HCCCH}	= 2.8
$\text{N}_3\text{P}_3\text{Cl}_4(\text{C}_2\text{H}_5)(\text{CH}_2\text{C}\equiv\text{CH})$	$-\text{CH}_2\text{CH}_3$	1.89 (br, m)	J_{HCCH}	= 7.5
	$-\text{CH}_2\text{CH}_3$	1.20 (d, t)	J_{PCCH}	= 21.3
	$-\text{CH}_2\text{C}\equiv\text{CH}$	2.80 (d, m)	J_{PCH}	= 15.2
	$-\text{CH}_2\text{C}\equiv\text{CH}$	2.20 (d, t)	J_{PCCCH}	= 6.8
			J_{HCCCH}	= 2.8
$\text{N}_3\text{P}_3\text{Cl}_4(\text{n-C}_3\text{H}_7)(\text{CH}_2\text{C}\equiv\text{CH})$	$-(\text{CH}_2)_2\text{CH}_3$	1.90 (br, m)		-
	$-(\text{CH}_2)_2\text{CH}_3$	1.10 (t)	J_{HCCH}	= 6.9
	$-\text{CH}_2\text{C}\equiv\text{CH}$	2.90 (d, m)	J_{PCH}	= 16.0
	$-\text{CH}_2\text{C}\equiv\text{CH}$	1.90 (u)	J_{HCCCH}	= 3.0
$\text{N}_3\text{P}_3\text{Cl}_4(\text{n-C}_4\text{H}_9)(\text{CH}_2\text{C}\equiv\text{CH})$	$-(\text{CH}_2)_3\text{CH}_3$	1.70 (br, m)		-
	$-(\text{CH}_2)_3\text{CH}_3$	1.10 (t)	J_{HCCH}	= 7.0
	$-\text{CH}_2\text{C}\equiv\text{CH}$	2.80 (d, m)	J_{PCH}	= 14.0
	$-\text{CH}_2\text{C}\equiv\text{CH}$	1.90 (u)	J_{HCCCH}	= 3.0
$\text{N}_3\text{P}_3\text{Cl}_4(\text{i-C}_3\text{H}_7)(\text{CH}_2\text{C}\equiv\text{CH})$	$-\text{CH}(\text{CH}_3)_2$	1.95 (m)	J_{HCCH}	= 6.0
	$-\text{CH}(\text{CH}_3)_2$	1.10 (d, d)	J_{PCCH}	= 18.0
	$-\text{CH}_2\text{C}\equiv\text{CH}$	2.80 (d, m)	J_{PCH}	= 14.0
	$-\text{CH}_2\text{C}\equiv\text{CH}$	2.10 (d, t)	J_{PCCCH}	= 6.9
			J_{HCCCH}	= 3.0

TABLE III (continued)

$N_3P_3Cl_4(i-C_4H_9)(CH_2C\equiv CH)$	$-CH_2CH(CH_3)_2$	2.00 (br, m)	-
	$-CH_2CH(CH_3)_2$	1.15 (d)	$J_{HCCH} = 7.0$
	$-CH_2C\equiv CH$	2.90 (d, m)	$J_{PCH} = 14.0$
	$-CH_2C\equiv CH$	1.90 (u)	$J_{HCCCH} = 3.0$
$N_3P_3Cl_4(t-C_4H_9)(CH_2C\equiv CH)$	$-C(CH_3)_3$	1.20 (d)	$J_{PCCH} = 18.0$
	$-CH_2C\equiv CH$	2.80 (d, m)	$J_{PCH} = 12.0$
	$-CH_2C\equiv CH$	2.10 (d, t)	$J_{PCCCH} = 6.2$
			$J_{HCCCH} = 2.6$
$N_3P_3Cl_4(C_3H_5)(CH_2C\equiv CH)$	$-CH_2CH=CH_2$	2.8 (u)	-
	$-CH_2CH=CH_2$	5.40 (br, m)	-
	$-CH_2C\equiv CH$	2.8 (u)	$J_{HCCCH} = 2.0$
	$-CH_2C\equiv CH$	2.20 (d, t)	$J_{PCCCH} = 6.5$
$N_3P_3Cl_4(CH_3)(CH=C=CH_2)$	$-CH_3$	1.70 (d, t)	$J_{PCH} = 15.1$
			$J_{PNPCH} = 2.5$
	$-CH=C=CH_2$	5.54 (d, m)	$J_{PCH} = 13.2$
	$-CH=C-CH_2$	5.16 (d, d)	$J_{PCCCH} = 12.6$
			$J_{HCCCH} = 7.0$
$N_3P_3Cl_4(C_2H_5)(CH=C=CH_2)$	$-CH_2CH_3$	1.93 (br, m)	$J_{HCCH} = 7.4$
	$-CH_2CH_3$	1.22 (d, t)	$J_{PCCH} = 22.0$
	$-CH=C=CH_2$	5.51 (d, m)	$J_{PCH} = 14.1$
	$-CH=C-CH_2$	5.15 (d, d)	$J_{PCCCH} = 12.3$
			$J_{HCCCH} = 6.6$

TABLE III (continued)

$N_3P_3Cl_4(\underline{n}-C_3H_7)(CH=C=CH_2)$	$-(\underline{CH_2})_2\underline{CH_3}$	1.80 (br,m)	-
	$-(\underline{CH_2})_2\underline{CH_3}$	1.20 (t)	$J_{HCCH} = 6.8$
	$-\underline{CH}=C=CH_2$	5.50 (d,m)	$J_{PCH} = 13.9$
	$-\underline{CH}=C=\underline{CH_2}$	5.10 (d,d)	$J_{PCCCH} = 12.0$
			$J_{HCCCH} = 6.9$
$N_3P_3Cl_4(\underline{n}-C_4H_9)(CH=C=CH_2)$	$-(\underline{CH_2})_3\underline{CH_3}$	1.70 (br,m)	-
	$-(\underline{CH_2})_3\underline{CH_3}$	1.20 (t)	$J_{HCCH} = 7.0$
	$-\underline{CH}=C=CH_2$	5.50 (d,m)	$J_{PCH} = 13.1$
	$-\underline{CH}=C=\underline{CH_2}$	5.13 (d,d)	$J_{PCCCH} = 12.2$
			$J_{HCCCH} = 6.4$
$N_3P_3Cl_4(\underline{i}-C_3H_7)(CH=C=CH_2)$	$-\underline{CH}(\underline{CH_3})_2$	1.95 (br,m)	$J_{HCCH} = 6.0$
	$-\underline{CH}(\underline{CH_3})_2$	1.10 (d,d)	$J_{PCCH} = 18.0$
	$-\underline{CH}=C=CH_2$	5.40 (d,m)	$J_{PCH} = 13.6$
	$-\underline{CH}=C=\underline{CH_2}$	5.10 (d,d)	$J_{PCCCH} = 12.0$
			$J_{HCCCH} = 6.3$
$N_3P_3Cl_4(\underline{i}-C_4H_9)(CH=C=CH_2)$	$-\underline{CH_2}\underline{CH}(\underline{CH_3})_2$	1.90 (br,m)	-
	$-\underline{CH_2}\underline{CH}(\underline{CH_3})_2$	1.10 (d)	$J_{HCCH} = 7.0$
	$-\underline{CH}=C=CH_2$	5.45 (d,m)	$J_{PCH} = 13.7$
	$-\underline{CH}=C=\underline{CH_2}$	5.10 (d,d)	$J_{PCCCH} = 12.0$
			$J_{HCCCH} = 6.5$
$N_3P_3Cl_4(\underline{t}-C_4H_9)(CH=C=CH_2)$	$-\underline{C}(\underline{CH_3})_3$	1.20 (d)	$J_{PCCH} = 19.0$
	$-\underline{CH}=C=CH_2$	5.45 (d,m)	$J_{PCH} = 13.4$
	$-\underline{CH}=C=\underline{CH_2}$	5.12 (d,d)	$J_{PCCCH} = 11.5$
			$J_{HCCCH} = 6.6$

TABLE III (continued)

$N_3P_3Cl_4(C_3H_5)(CH=C=CH_2)$	$-CH_2CH=CH_2$	2.50 (d,m)	$J_{PCH} = 16.0$
	$-CH_2CH=CH_2$	5.4 (u)	-
	$-CH=C=CH_2$	5.4 (u)	-
$N_3P_3Cl_4(CH_3)(C\equiv CCH_3)$	$-CH_3$	1.70 (d,t)	$J_{PCH} = 16.0$
			$J_{PNPCH} = 3.0$
	$-C\equiv C-CH_3$	1.90 (d)	$J_{PCCCH} = 4.0$
$N_3P_3Cl_4(C_2H_5)(C\equiv CCH_3)$	$-CH_2CH_3$	1.80 (br,m)	$J_{HCCH} = 6.0$
	$-CH_2CH_3$	1.10 (d,t)	$J_{PCCH} = 22.0$
	$-C\equiv CCH_3$	2.00 (d)	$J_{PCCCH} = 4.0$
$N_3P_3Cl_4(n-C_3H_7)(C\equiv CCH_3)$	$-(CH_2)_2CH_3$	1.90 (br,m)	-
	$-(CH_2)_2CH_3$	1.10 (t)	$J_{HCCH} = 7.0$
	$-C\equiv CCH_3$	2.10 (d)	$J_{PCCCH} = 3.9$
$N_3P_3Cl_4(n-C_4H_9)(C\equiv CCH_3)$	$-(CH_2)_3CH_3$	1.80 (br,m)	-
	$-(CH_2)_3CH_3$	1.10 (t)	$J_{HCCH} = 7.0$
	$-C\equiv CCH_3$	2.10 (d)	$J_{PCCCH} = 3.9$
$N_3P_3Cl_4(i-C_3H_7)(C\equiv CCH_3)$	$-CH(CH_3)_2$	1.90 (m)	$J_{HCCH} = 7.0$
	$-CH(CH_3)_2$	1.20 (d,d)	$J_{PCCH} = 21.0$
	$-C\equiv CCH_3$	2.10 (d)	$J_{PCCCH} = 4.0$
$N_3P_3Cl_4(i-C_4H_9)(C\equiv CCH_3)$	$-CH_2CH(CH_3)_2$	2.00 (m)	-
	$-CH_2CH(CH_3)_2$	1.07 (d)	$J_{HCCH} = 6.4$
	$-C\equiv CCH_3$	2.02 (d)	$J_{PCCCH} = 3.5$
$N_3P_3Cl_4(t-C_4H_9)(C\equiv CCH_3)$	$-C(CH_3)_3$	1.20 (d)	$J_{PCCH} = 20.0$
	$-C\equiv CCH_3$	2.00 (d)	$J_{PCCCH} = 4.0$

TABLE III (continued)

$N_3P_3Cl_4(C_3H_5)(C\equiv CCH_3)$	$-CH_2CH=CH_2$	2.75 (d,m)	$J_{PCH} = 12.0$
			$J_{PNPCH} = 2.1$
	$-CH_2CH=CH_2$	5.40 (br,m)	$J_{HCCH} = 7.0$
$N_3P_3Cl_4(CH_3)(CH_2C\equiv CCH_3)$	$-C\equiv CCH_3$	2.10 (d)	$J_{PCCCH} = 4.0$
	$-CH_3$	1.71 (d,t)	$J_{PCH} = 14.3$
			$J_{PNPCH} = 2.6$
	$-CH_2C\equiv CCH_3$	2.77 (d,t,m)	$J_{PCH} = 14.3$
			$J_{PNPCH} = 2.1$
	$-CH_2C\equiv CCH_3$	1.84 (d,t)	$J_{HCCCCH} = 2.6$
			$J_{PCCCCH} = 6.6$

^a d = doublet, t = triplet, br = broad, m = multiplet, u = unresolved due to peak overlap.

^b Coupling constants unresolved if not listed; no attempt was made to determine absolute signs of coupling constants.

TABLE IV. DIALKYLPHOSPHAZENES. ^{13}C NMR DATA

COMPOUND	CHEMICAL SHIFT (ppm) ^{a, b}		COUPLING CONSTANTS (Hz) ^c	
			J _{P-C}	J _{PNPC}
N ₃ P ₃ Cl ₄ (CH ₃) (CH ₂ C≡CH)	-CH ₃	17.6 (d, t)	98.5	4.2
	-CH ₂ C≡CH	25.5 (d, t)	88.8	2.7
	-CH ₂ C≡CH	73.6 (d)	14.8	-
	-CH ₂ C≡CH	73.9 (d)	9.5	-
N ₃ P ₃ Cl ₄ (C ₂ H ₅) (CH ₂ C≡CH)	-CH ₂ CH ₃	23.9 (d, t)	95.5	3.8
	-CH ₂ CH ₃	4.8 (d)	6.9	-
	-CH ₂ C≡CH	24.2 (d, t)	84.7	2.6
	-CH ₂ C≡CH	73.0 (d)	13.8	-
	-CH ₂ C≡CH	73.6 (d)	9.4	-
N ₃ P ₃ Cl ₄ (n-C ₃ H ₇) (CH ₂ C≡CH)	-CH ₂ CH ₂ CH ₃	32.7 (d, t)	94.6	4.1
	-CH ₂ CH ₂ CH ₃	14.7 (d)	5.7	-
	-CH ₂ CH ₂ CH ₃	14.9 (d)	17.6	-
	-CH ₂ C≡CH	24.8 (d, t)	87.3	2.8
	-CH ₂ C≡CH	73.2 (d)	14.2	-
	-CH ₂ C≡CH	73.6 (d)	9.5	-
N ₃ P ₃ Cl ₄ (n-C ₄ H ₉) (CH ₂ C≡CH)	-CH ₂ CH ₂ CH ₂ CH ₃	30.3 (d, t)	95.1	4.0
	-CH ₂ CH ₂ CH ₂ CH ₃	22.9 (d)	5.5	-
	-CH ₂ CH ₂ CH ₂ CH ₃	23.3 (d)	16.6	-
	-CH ₂ CH ₂ CH ₂ CH ₃	13.4 (s)	-	-
	-CH ₂ C≡CH	24.8 (d, t)	82.1	2.8
	-CH ₂ C≡CH	73.2 (d)	14.0	-
	-CH ₂ C≡CH	73.5 (d)	9.6	-

TABLE IV (continued)

$N_3P_3Cl_4(i-C_3H_7)(CH_2C\equiv CH)$	$\underline{CH}(CH_3)_2$	29.1 (d,t)	93.3	3.5
	$\underline{CH}(CH_3)_2$	14.5 (d)	3.1	-
	$\underline{CH_2}C\equiv CH$	22.1 (d,t)	84.5	2.6
	$\underline{CH_2}C\equiv CH$	73.1 (d)	14.2	-
	$\underline{CH_2}C\equiv CH$	73.5 (d)	9.0	-
$N_3P_3Cl_4(i-C_4H_9)(CH_2C\equiv CH)$	$\underline{CH_2}CH(CH_3)_2$	39.0 (d,t)	94.0	3.8
	$\underline{CH_2}CH(CH_3)_2$	23.3 (d)	5.1	-
	$\underline{CH_2}CH(CH_3)_2$	24.2 (d)	10.2	-
	$\underline{CH_2}C\equiv CH$	25.6 (d,t)	86.6	2.2
	$CH_2C\equiv CH$	73.3 (d)	14.5	-
	$\underline{CH_2}C\equiv CH$	73.7 (d)	9.1	-
$N_3P_3Cl_4(t-C_4H_9)(CH_2C\equiv CH)$	$\underline{C}(CH_3)_3$	34.2 (d,t)	90.7	3.3
	$\underline{C}(CH_3)_3$	23.3 (s)	-	-
	$\underline{CH_2}C\equiv CH$	19.4 (d,t)	80.5	2.2
	$\underline{CH_2}C\equiv CH$	73.4 (d)	15.6	-
	$\underline{CH_2}C\equiv CH$	73.8 (d)	8.2	-
$N_3P_3Cl_4(C_3H_5)(CH_2C\equiv CH)$	$\underline{CH_2}CH=CH_2$	36.3 (d,t)	91.1	3.3
	$\underline{CH_2}CH=CH_2$	124.8 (d)	12.2	-
	$\underline{CH_2}CH=CH_2$	123.1 (d)	13.7	-
	$\underline{CH_2}C\equiv CH$	24.1 (d,t)	89.3	3.1
	$\underline{CH_2}C\equiv CH$	72.9 (d)	13.9	-
	$\underline{CH_2}C\equiv CH$	73.8 (d)	9.8	-
$N_3P_3Cl_4(CH_3)(CH=C=CH_2)$	$\underline{CH_3}$	20.0 (d,t)	104.1	5.4
	$\underline{CH}=C=CH_2$	86.2 (d,t)	131.7	2.9
	$\underline{CH}=C=CH_2$	212.9 (s)	-	-
	$\underline{CH}=C=CH_2$	78.0 (d)	15.6	-

TABLE IV (continued)

$N_3P_3Cl_4(C_2H_5)(CH=C=CH_2)$	$-\underline{CH}_2CH_3$	25.8 (d,t)	101.2	4.4
	$-\underline{CH}_2\underline{CH}_3$	4.8 (d)	6.2	-
	$-\underline{CH}=C=CH_2$	84.6 (d,t)	129.1	2.8
	$-\underline{CH}=\underline{C}=CH_2$	213.3 (s)	-	-
	$-\underline{CH}=C=\underline{CH}_2$	77.6 (d)	14.6	-
$N_3P_3Cl_4(\underline{n}-C_3H_7)(CH=C=CH_2)$	$-\underline{CH}_2CH_2CH_3$	34.6 (d,t)	100.0	4.7
	$-\underline{CH}_2\underline{CH}_2CH_3$	14.6 (d)	5.7	-
	$-\underline{CH}_2CH_2\underline{CH}_3$	14.8 (d)	16.9	-
	$-\underline{CH}=C=CH_2$	85.1 (d,t)	128.6	3.2
	$-\underline{CH}=\underline{C}-CH_2$	213.2 (s)	-	-
	$-\underline{CH}=C=\underline{CH}_2$	77.7 (d)	14.4	-
$N_3P_3Cl_4(\underline{n}-C_4H_9)(CH=C=CH_2)$	$-\underline{CH}_2CH_2CH_2CH_3$	32.2 (d,t)	100.2	4.5
	$-\underline{CH}_2\underline{CH}_2CH_2CH_3$	22.8 (d)	4.6	-
	$-\underline{CH}_2CH_2\underline{CH}_2CH_3$	23.1 (d)	17.9	-
	$-\underline{CH}_2CH_2CH_2\underline{CH}_3$	13.4 (s)	-	-
	$-\underline{CH}=C=CH_2$	85.0 (d,t)	128.2	3.0
	$-\underline{CH}=\underline{C}=CH_2$	213.1 (s)	-	-
	$-\underline{CH}=C=\underline{CH}_2$	77.6 (d)	14.8	-
$N_3P_3Cl_4(\underline{i}-C_3H_7)(CH=C=CH_2)$	$-\underline{CH}(CH_3)_2$	30.9 (d,t)	94.4	4.3
	$-\underline{CH}(\underline{CH}_3)_2$	14.3 (d)	2.7	-
	$-\underline{CH}=C=CH_2$	83.0 (d,t)	125.6	3.1
	$-\underline{CH}=\underline{C}=CH_2$	213.0 (s)	-	-
	$-\underline{CH}=C=\underline{CH}_2$	77.4 (d)	14.2	-

TABLE IV (continued)

$N_3P_3Cl_4$ ($i-C_4H_9$) ($CH=C=CH_2$)	$-CH_2CH(CH_3)_2$	41.1 (d,t)	99.7	4.9
	$-CH_2\overline{CH}(CH_3)_2$	23.2 (d)	4.8	-
	$-CH_2CH(\overline{CH}_3)_2$	24.2 (d)	10.4	-
	$-\overline{CH}=C=CH_2$	85.9 (d,t)	128.2	2.4
	$-CH=\overline{C}=CH_2$	213.1 (s)	-	-
	$-CH=C=\overline{CH}_2$	77.8 (d)	14.6	-
$N_3P_3Cl_4$ ($t-C_4H_9$) ($CH=C=CH_2$)	$-\overline{C}(CH_3)_3$	34.5 (d,t)	97.1	4.0
	$-C(\overline{CH}_3)_3$	22.6 (s)	-	-
	$-\overline{CH}=C=CH_2$	81.1 (d,t)	122.6	3.0
	$-CH=\overline{C}=CH_2$	214.3 (s)	-	-
	$-CH=C=\overline{CH}_2$	77.1 (d)	13.5	-
$N_3P_3Cl_4$ (C_3H_5) ($CH=C=CH_2$)	$-\overline{CH}_2CH=CH_2$	38.2 (d,t)	96.5	4.2
	$-CH_2\overline{CH}=CH_2$	124.8 (d)	12.2	-
	$-CH_2CH=\overline{CH}_2$	122.9 (d)	13.6	-
	$-\overline{CH}=C=CH_2$	84.7 (d,t)	131.9	3.7
	$-CH=\overline{C}=CH_2$	213.4 (s)	-	-
	$-CH=C=\overline{CH}_2$	77.9 (d)	15.4	-
$N_3P_3Cl_4$ (CH_3) ($C\equiv CCH_3$)	$-\overline{CH}_3$	23.2 (d,t)	119.0	6.3
	$-\overline{C}\equiv CCH_3$	74.3 (d,t)	213.9	3.7
	$-C\equiv\overline{C}CH_3$	101.8 (d,t)	43.4	1.3
	$-C\equiv C\overline{CH}_3$	4.6 (d)	3.9	-
$N_3P_3Cl_4$ (C_2H_5) ($C\equiv CCH_3$)	$-\overline{CH}_2CH_3$	28.9 (d,t)	115.1	5.4
	$-CH_2\overline{CH}_3$	4.9 (d)	5.3	-
	$-\overline{C}\equiv CCH_3$	73.9 (d,t)	214.2	3.8
	$-C\equiv\overline{C}CH_3$	102.3 (d,t)	40.4	1.2
	$-C\equiv C\overline{CH}_3$	3.9 (d)	3.8	-

TABLE IV (continued)

$N_3P_3Cl_4$ ($n-C_3H_7$) ($C\equiv CCH_3$)	$-CH_2CH_2CH_3$	37.5 (d,t)	113.5	5.4
	$-CH_2CH_2CH_3$	14.5 (d)	4.6	-
	$-CH_2CH_2CH_3$	14.8 (d)	16.3	-
	$-C\equiv CCH_3$	74.5 (d,t)	212.6	3.7
	$-C\equiv CCH_3$	102.7 (d,t)	40.5	1.3
	$-C\equiv CCH_3$	4.7 (d)	3.7	-
$N_3P_3Cl_4$ ($n-C_4H_9$) ($C\equiv CCH_3$)	$-CH_2CH_2CH_2CH_3$	35.3 (d,t)	120.0	5.5
	$-CH_2CH_2CH_2CH_3$	23.1 (d)	5.3	-
	$-CH_2CH_2CH_2CH_3$	23.4 (d)	13.6	-
	$-CH_2CH_2CH_2CH_3$	13.4 (s)	-	-
	$-C\equiv CCH_3$	74.3 (d,t)	216.0	3.5
	$-C\equiv CCH_3$	102.0 (d,t)	40.5	1.1
	$-C\equiv CCH_3$	3.8 (d)	3.5	-
$N_3P_3Cl_4$ ($i-C_3H_7$) ($C\equiv CCH_3$)	$-CH(CH_3)_2$	32.9 (d,t)	113.3	5.1
	$-CH(CH_3)_2$	14.1 (d)	2.1	-
	$-C\equiv CCH_3$	74.5 (d,t)	212.6	3.7
	$-C\equiv CCH_3$	102.6 (d,t)	39.0	1.2
	$-C\equiv CCH_3$	3.8 (d)	3.7	-
$N_3P_3Cl_4$ ($i-C_4H_9$) ($C\equiv CCH_3$)	$-CH_2CH(CH_3)_2$	44.1 (d,t)	113.1	5.2
	$-CH_2CH(CH_3)_2$	23.1 (d)	4.5	-
	$-CH_2CH(CH_3)_2$	24.1 (d)	11.9	-
	$-C\equiv CCH_3$	74.2 (d,t)	214.0	3.7
	$-C\equiv CCH_3$	101.8 (d,t)	40.9	1.0
	$-C\equiv CCH_3$	4.7 (d)	3.7	-

TABLE IV (continued)

$N_3P_3Cl_4(t-C_4H_9)(C\equiv CCH_3)$	$-C(CH_3)_3$	34.5 (d,t)	110.0	4.3
	$-C(CH_3)_3$	22.2 (s)	-	-
	$-C\equiv CCH_3$	71.6 (d,t)	200.6	3.6
	$-C\equiv CCH_3$	102.5 (d,t)	36.2	1.4
	$-C\equiv CCH_3$	4.6 (d)	3.5	-
$N_3P_3Cl_4(C_3H_5)(C\equiv CCH_3)$	$-CH_2CH=CH_2$	41.0 (d,t)	110.9	4.3
	$-CH_2CH=CH_2$	124.4 (d)	12.7	-
	$-CH_2CH=CH_2$	123.1 (d)	15.6	-
	$-C\equiv CCH_3$	73.4 (d,t)	218.1	4.1
	$-C\equiv CCH_3$	102.6 (d,t)	41.7	1.5
	$-C\equiv CCH_3$	4.7 (d)	3.7	-
$N_3P_3Cl_4(CH_3)(CH_2C\equiv CCH_3)$	$-CH_3$	18.4 (d,t)	97.7	5.2
	$-CH_2C\equiv CCH_3$	26.3 (d,t)	88.4	1.9
	$-CH_2C\equiv CCH_3$	67.8 (d)	16.2	-
	$-CH_2C\equiv CCH_3$	81.7 (d)	9.2	-
	$-CH_2C\equiv CCH_3$	3.73 (d)	3.5	-

^a d = doublet, t = triplet, m = multiplet

^b Peak assignments were made directly, by the use of ORD techniques, or by comparison to spectra of similar compounds.⁶ In the few cases where accidental peak overlap occurred, peak assignments were made from consideration of the spectrum of the same compound obtained at higher field strength.⁴¹

Figure 1. Changes in the ^{31}P NMR spectrum following addition of methyllithium to methylhydridotetrachlorocyclotriphosphazene (III, $\text{R} = \text{CH}_3$) at -70°C . The differences between spectra a, b, and c are discussed in the text.

Figure 2. Changes in the ^{31}P NMR spectrum during rearrangement of the prop-2-ynyl substituted phosphazene (VI, $\text{R} = \text{CH}_3$) to the prop-1,2-dienyl derivative to the prop-1-ynyl compound, initiated by methyllithium.

Figure 3. ^{31}P NMR spectral changes following the addition of a small quantity of methyllithium to a solution of the prop-1,2-dienyl substituted phosphazene (VI, $\text{R} = \text{CH}_3$).

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